

Femtochemistry of Little Men

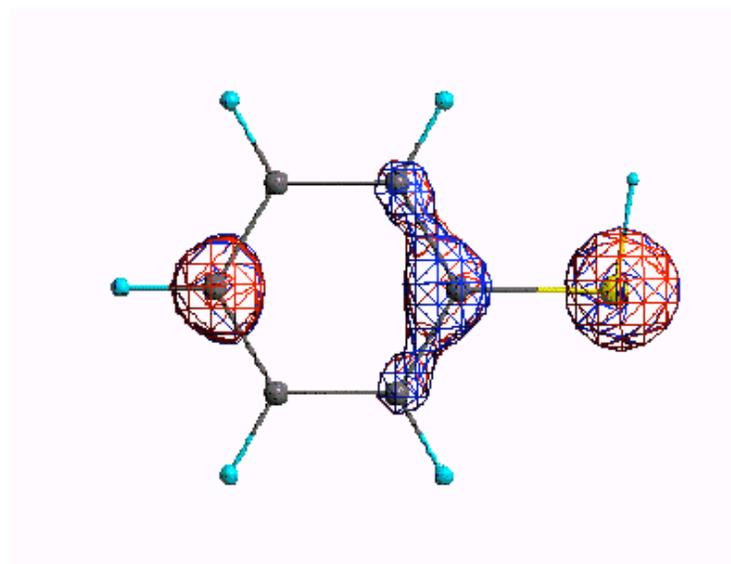
?

Chemical reactions observed in the nanosecond time range which reflect femtosecond events

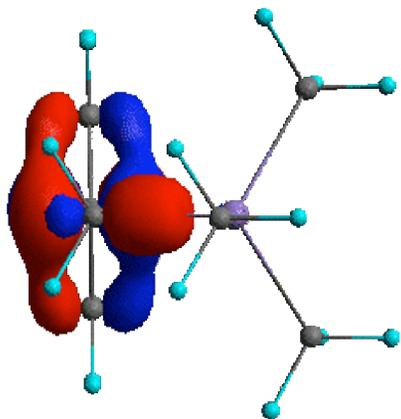
Ortwin Brede and Sergej Naumov

Thiophenol: rotation of the –SH group around the aromatic moiety,

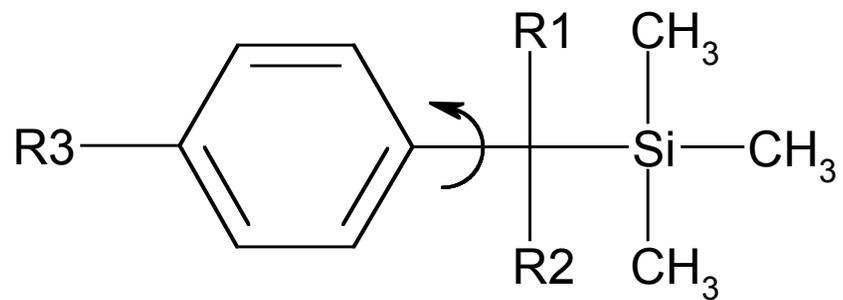
time for one rotation: 300 fs



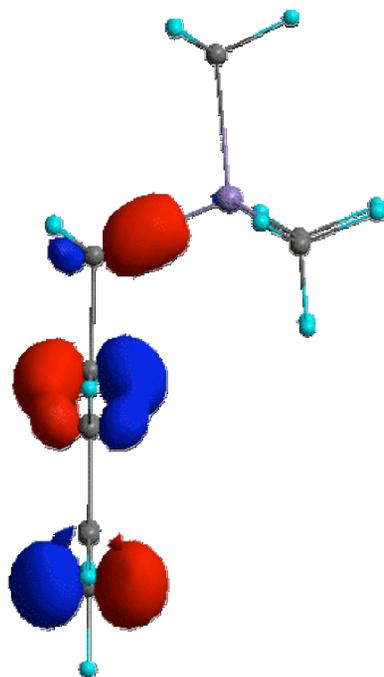
-S:H vibration within 13 fs



~ 1 ps rotation in benzyltrimethylsilanes



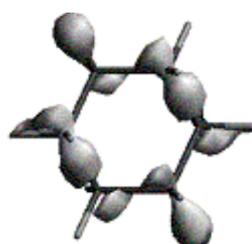
R = H



Parent solvent radical cations as electron acceptors in the free electron transfer (FET)



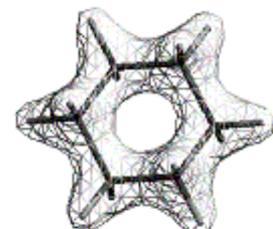
n-heptane



cyclohexane

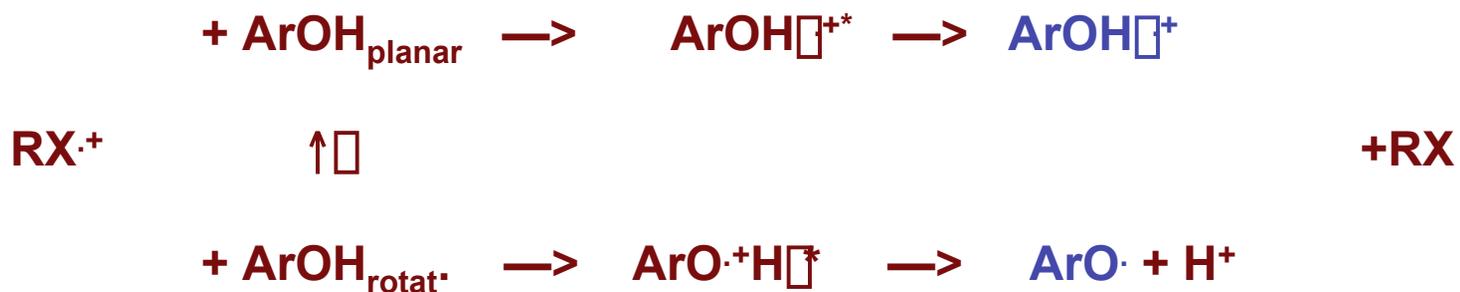


n-butyl chloride



Can any reaction reflect the fs molecule dynamics ?

- Free electron transfer from donors to parent solvent cations
- Example: phenols, thiophenols, selenols, aromatic amines etc.
- Conditions: two different product radical cations



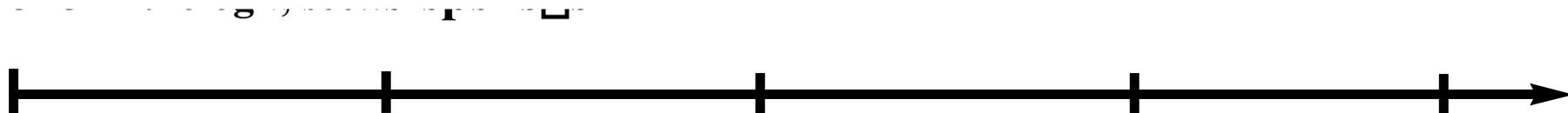
Time range of processes relevant in FET

Principal physical processes

electron fluctuation, aromatics

molecular motions
 vibration rotation (conformers)

bimolecular diffusion-controlled



FET: electron jump in the super molecule

deprotonation of $\text{ArO}^{\bullet}\text{H}$ perpendicular

relaxation of excited $\text{ArOH}^{\bullet*}$

gross reaction $\text{BuCl}^{\bullet} + \text{ArOH}$

deprotonation of ArOH^{\bullet} planar

Free electron transfer

Conditions for the identification of rotation states by free electron transfer

- FET: the electron jumps in the **first encounter**
- Molecular oscillations create different „conformers“ with different electron distribution
- In ionization, the diversity of conformers produces at least two different molecular cations which can be distinguished (by their properties, e.g. stability)
- This process depends on the mobility of the substituent
- Good leaving groups: H^+ , Me_3Si^+ , Me_3C^+ etc.
- **Paradox phenomenon: bimolecular reaction in the ns time range reflects fs oscillations (rotation)**